

553,788

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
25 November 2004 (25.11.2004)

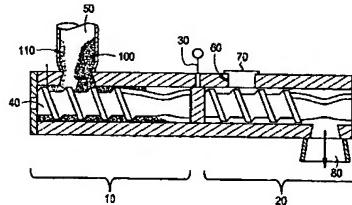
PCT

(10) International Publication Number
WO 2004/101674 A1

- (51) International Patent Classification⁷: **C08L 23/16**, C08J 5/18, C08F 2/00, 210/16
- (72) Inventors; and
(75) Inventors/Applicants (*for US only*): MICHIE, William, J., Jr. [US/US]; 9111 South Fitzgerald Way, Missouri City, TX 77459 (US). NEUBAUER, Anthony, C. [US/US]; 5 Gilman Drive, Piscataway, NJ 08854 (US). COBLER, Brad, A. [US/US]; 209 Zinnia, Lake Jackson, TX 77566 (US). BAKER, Carl, F. [US/US]; 217 Dewberry Drive, Lake Jackson, TX 77566 (US).
- (21) International Application Number: **PCT/US2004/013975**
- (22) International Filing Date: 5 May 2004 (05.05.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 60/469,665 12 May 2003 (12.05.2003) US
- (71) Applicant (*for all designated States except US*): DOW GLOBAL TECHNOLOGIES INC [US/US]; Washington Street, 1790 Building, Midland, MI 48674 (US).
- (74) Agent: CAVENDER, Carol, J.; The Dow Chemical Company, Intellectual Property Section, P.O. Box 1967, Midland, MI 48674-1967 (US).
- (81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,

[Continued on next page]

(54) Title: POLYMER COMPOSITION AND PROCESS TO MANUFACTURE HIGH MOLECULAR WEIGHT-HIGH DENSITY POLYETHYLENE AND FILM THEREFROM



(57) Abstract: The present invention includes a multimodal polyethylene composition has (1) a density of at least about 0.940 g/cm³ as measured by ASTM Method D-1505; (2) a melt flow index (I_5) of from about 0.2 to about 1.5 g/10 min (as measured by ASTM D-1238, measured at 190 °C and 5 kilograms); (3) a melt flow index ratio (I_2/I_5) of from about 20 to about 50; (4) a molecular weight distribution, M_w/M_n , of from about 20 to about 40; (5) a bubble stability measured on specified equipment according to specified conditions for a film of about 6×10^{-6} m thickness of at least about 1.22 m/s line speed, at least about 45 kg/hr (0.013 kg/sec) output rate, or at least about 0.5 lb/hr/rpm (0.0000011 kg/s/rps) specific output rate or a combination thereof; the composition comprising; and (6) a dart impact on 12.5 micron (1.25×10^{-5} m) film of at least 300 g; measured according to ASTM 1709, Method A; (A) a high molecular weight fraction which; (a) is present in an amount of from about 30 to about 70 weight percent (based on the total weight of the composition); (b) has a density of at least about 0.860 g/cm³ as measured by ASTM D-1505; (c) has a melt flow index (I_2) of from about 0.01 to about 50 g/10 min (as measured by ASTM D-1238, measured at 190 °C and 21.6 kilograms); and (d) a melt flow index ratio (I_2/I_5) of from about 6 to about 12; and (B) a low molecular weight fraction which; (a) is present in an amount of from about 30 to about 70 weight percent (based on the total weight of the composition); (b) has a density of at least about 0.900 g/cm³ as measured by ASTM D-1505; (c) has a melt flow index (I_2) of from about 0.5 to about 3000 g/10 min (as measured by ASTM D-1238, measured at 190 °C and 2.16 kilograms); (d) a melt flow index ratio (I_2/I_5) of from about 5 to about 15; and (e) is prepared using a mole ratio of alpha olefin to ethylene of less than or equal to about 0.001:1. The invention also includes a process for producing a multimodal ethylene polymer, which process comprises the following steps: (1) contacting in a first gas phase fluidized bed reactor under polymerization conditions and at a temperature of from about 70 °C to about 110 °C, a supported titanium magnesium catalyst precursor, cocatalyst, and a gaseous composition, the gaseous composition having; (i) a mole ratio of alpha-olefin to ethylene of from about 0.01:1 to about 0.8:1; and optionally (ii) a mole ratio of hydrogen to ethylene of from about 0.001:1 to about 0.3:1, to produce a high molecular weight polymer(HMW); and (2) transferring the HMW polymer from step 1 to a second gas phase fluidized bed reactor under polymerization conditions and at a temperature of from about 70 °C to about 110 °C, with a gaseous composition having; (i) a mole ratio of alpha-olefin to ethylene of from about 0.0005:1 to about 0.01:1; and (ii) a mole ratio of hydrogen (if present) to ethylene of from about 0.01:1 to about 3:1 to form a polymer blend.

WO 2004/101674 A1

[Continued on next page]



MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

- (84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI,

SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

product; and (3) melting the polymer blend product in an extruder having a mixer vent wherein; (ii) the mixture vent has an oxygen concentration of from about 0.05 to about 6 volume percent oxygen in nitrogen; and (ii) the extrusion temperature is sufficient to melt the polymer and achieve tailoring in the presence of oxygen; and (4) passing the molten polymer blend through one or more active screens, wherein in the 5 case of two or more active screens, the screens are positioned in series, each active screen having a micron retention size of from about 2 to about 70, at a mass flux of about 1.0 to about 20 kg/s/m²) to form a screened molten polymer blend. The composition is preparable by the process and is preferably prepared by the process. The resin exhibits improved extrusion processing at high commercial line speeds, while exhibiting an excellent balance of 10 bubble stability, dart drop, and FAR, as well as outstanding NCLS with good flexural modulus.